Solid Phase extracted metal distributions collected on the US GEOTRACES GP17- ANT expedition aboard R/V Nathaniel B. Palmer (cruise NBP24-01) in the Southern Ocean across the Amundsen Sea from December 2023 to January 2024

Website: https://www.bco-dmo.org/dataset/1001113
Data Type: Cruise Results
Version: 1
Version Date: 2026-06-16

Project
» Collaborative Research: US GEOTRACES GP-17-ANT: Molecular speciation of trace element-ligand complexes in the Southern Ocean and Antarctic shelf (GP17-ANT Trace element-ligand complexes)

Contributors	Affiliation	Role
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Abstract
Molecular speciation affects the solubility, bioavailability, toxicity, scavenging and regeneration rates, and water column residence times of trace elements in the ocean. The molecular speciation of trace elements is what microbes "sense" and respond to. In this dataset, we report the speciation of iron, copper, zinc, and nickel in water samples collected during the US GEOTRACES GP17-ANT expedition from Punta Arenas, Chile to Lyttelton, New Zealand. Trace metals complexed with oceanic dissolved organic matter were filtered, preconcentrated, and purified onto hydrophobic resins for solid-phase extraction, and recovered with organic solvent. The captured trace element organic complexes were then characterized and quantified by liquid chromatography coupled to inductively coupled mass spectrometry.

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Coverage

Location: Amundsen Sea Sector of the Antarctic Continental Margin
Spatial Extent: **N**:-66.97744 **E**:-99.68365 **S**:-74.38082 **W**:-133.02246
Temporal Extent: 2023-12-08 - 2024-01-13

Methods & Sampling

Sample collection and preparation:
Each water sample was filtered directly from the trace metal clean GTC rosette/Go-Flo bottle sampler through a

0.45 micrometer (µm) Supor membrane filter (25 millimeters (mm)) or 0.2 µm Pall Acropak-200 Supor cartridge into a trace metal grade acid-cleaned 4-liter (L) polycarbonate bottles. Samples for solid phase extracted trace element ligands (TELs) were pumped at 20 milliliters per minute (mL/min) through Bond-Elut ENV solid phase extraction (SPE) columns (1 gram (g), 6 mL, P/N 12255012, Agilent Technologies) that had been previously activated by passing 6 mL each of distilled methanol (MeOH, Optima LCMS grade, Fisher Scientific), 0.1% HCl (VWR chemical, Aristar Ultra grade), and ultrapure water (qH_2O, 18.2 MΩ) through the column. SPE columns were frozen (-20 degrees Celsius (°C)) immediately after sample collection and returned to the laboratory for processing.

Siderophore Processing:
SPE columns were thawed and concentrated TELs were then eluted with 10 mL distilled MeOH into 15 mL trace metal clean polypropylene tubes. Process blanks were prepared in parallel by eluting activated SPE columns with 10 mL MeOH. The methanol fraction was collected as the process blank. The eluted sample was concentrated down to ~1000 microliters (µL) by vacuum centrifugal concentrator (CentrIVap Evaporating System, LABCONCO).

A 10 µL stock solution of 100 micromolar (µM) cyanocobalamin was added to each sample as an internal standard.

Quantitative analyses of siderophores:
Chromatographic analyses were performed on a bioinert Dionex Ultimate 3000 liquid chromatograph (LC) system fitted with a loading pump, a low flow pump, and a 10-port switching valve. Full loop (50 µL) samples were injected using the 50 µL sample loop, then separated using a BEH C18 column (ACQUITY UPLC BEH C18, 130A^{o}, 1.7 µm, 2.1 mm X 50 mm, P/N 186002350, Waters) connected with a 5 mm guard column (ACQUITY UPLC BEH C18 VanGuard, 130A^{o}, 1.7 µm, 2.1 mm X 5 mm, P/N 186003975, Waters) by the low flow pump at 50 µL/min. 5 millimolar (mM) ammonium formate in Milli-Q water and LC-MS-grade methanol were used as solvents A and B, respectively. Samples were separated using a 40 minute gradient flow (95% A/ 5% B to 5% A/ 95% B) followed by 9 minute washout at 95% B. Meanwhile, the loading pump was used to supply an internal standard (4 parts per billion (ppb) Indium in 1% HNO3 as solvent C) at a constant rate and maintain 26% of total organic (LC-MS grade MeoH) flow by mixing loading pump flow (150 µL/min) and low flow (50 µL) post-column before infusing into the ICPMS.

The combined flow from the LC (200 µL/min) was analyzed using a Thermo Scientific iCAP Q ICPMS fitted with a perfluoroalkoxy micronebulizer (PFA-ST, Elemental Scientific), and a cyclonic spray chamber cooled to 0 °C. Measurements were made in kinetic energy discrimination (KED) mode, with a helium collision gas flow of 4-4.5 mL/min to minimize isobaric interferences. Oxygen was introduced into the sample carrier gas at 25 mL/min to prevent the formation of reduced organic deposits onto the ICPMS skimmer and sampling cones.

The metal detector response was calibrated using standards, 10 ppb, 20 ppb, 50 ppb, 100 ppb, and 200 ppb, prepared from a commercial stock solution (InorganicVentures). These standards were analyzed using a method similar to other samples, but no column was connected and eluted with 5% of solvent B and 95% of solvent A for five minutes. A plot of the metal peak areas against concentration yielded a linear relationship (r^2 ~0.99) for the response of the ICPMS detector as calibration curve. Calibrations and process blanks were made for every 10-20 samples analyzed, with only small changes (RSD ~30%) were observed in the slope of the calibration relationship over the course of the two years of sample analysis. Concentrations of TELs in each sample were calculated by integrating the metal peak area (detector response) of interested time range and using appropriate calibration curve for the peak area.

Data Processing Description

Raw intensity ICPMS data over time were exported in '.csv' format. We used a custom Python script (v3.10.9) to integrate peak areas and calculate concentrations based on an external calibration curve (link: https://github.com/tanil07/LC-ICPMS-integration-and-combining-with-metadata; DOI: 10.5281/zenodo.18486409).

BCO-DMO Processing Description

- Loaded data from "GP17 ANT DSPEMETAL Concentration 02122026.xlsx" (sheet "combined_odvdata_all_with_meta") into the BCO-DMO processing system.
- Renamed column "GEOTRACES ID" to "GEOTRACES_ID".
- Combined Date (format "%Y/%m/%d") and Time (format "%H:%M:%S") fields in UTC to create new datetime column "ISO_DateTime_UTC" (format "%Y-%m-%dT%H:%M:%SZ").
- Saved the final file as "1001113_v1_gp17_dspe_metal.csv".

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Data Files

File
1001113_v1_gp17_dspe_metal.csv (Comma Separated Values (.csv), 53.72 KB) MD5:4eac05a2995e2ebc578115af64b386f4 Primary data file for dataset ID 1001113, version 1

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Related Publications

tanil07. (2026). tanil07/LC-ICPMS-integration-and-combining-with-metadata: Integrate LC-ICMS (Version V1.0) [Computer software]. Zenodo. https://doi.org/10.5281/zenodo.18486409
Software

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Parameters

Parameter	Description	Units
Station	Cruise station identifier	Unitless
GEOTRACES_ID	Unique GEOTRACES identifier for each water-column sample	Unitless
Cast	Cast number	Unitless
ISO_DateTime_UTC	Sample collection date and time (UTC) in ISO 8601 format	units
Date	Sample collection date	Unitless
Time	Sample collection time (UTC)	Unitless
Event	Event number	Unitless
Latitude	Latitude of sampling event; negative = south	decimal degrees
Longitude	Longitude of sampling event; negative = west	decimal degrees
Depth	Sample collection depth	meter (m)
TotalFeLigands_56_DSPEENV_CONC_BOTTLE	Total SPE dissolved iron concentration in nM [integrated retention time interval 6-50 min]	nanomole per litre (nM)
HydrophilicFeLigands_56_DSPEENV_CONC_BOTTLE	Hydrophilic SPE dissolved iron concentration in nM [integrated retention time interval 6-33 min]	nanomole per litre (nM)
HydrophobicFeLigands_56_DSPEENV_CONC_BOTTLE	Hydrophobic SPE dissolved iron concentration in nM [integrated retention time interval 33-50 min]	nanomole per litre (nM)
TotalNiLigands_60_DSPEENV_CONC_BOTTLE	Total SPE dissolved Nickel concentration in nM [integrated retention time interval 6-50 min]	nanomole per litre (nM)
TotalCuLigands_63_DSPEENV_CONC_BOTTLE	Total SPE dissolved Copper concentration in nM [integrated retention time interval 6-50 min]	nanomole per litre (nM)
TotalZnLigands_66_DSPEENV_CONC_BOTTLE	Total SPE dissolved Zinc concentration in nM [integrated retention time interval 6-50 min]	nanomole per litre (nM)

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Instruments

Dataset-specific Instrument Name	vacuum centrifugal concentrator (CentrIVap Evaporating System, LABCONCO)
Generic Instrument Name	Concentrator Device
Generic Instrument Description	A concentrator is a device designed to increase the weight per unit volume of a substance. This category includes vacuum centrifuge concentrator, which include a vacuum chamber within which a centrifuge rotor is mounted for spinning a plurality of vials containing a solution at high speed while subjecting the solution to a vacuum condition for concentration and evaporation. Alternative names: sample concentrator; speed vacuum; speed vac.

Dataset-specific Instrument Name	GTC rosette/Go-Flo bottle sampler
Generic Instrument Name	GO-FLO Bottle
Generic Instrument Description	GO-FLO bottle cast used to collect water samples for pigment, nutrient, plankton, etc. The GO-FLO sampling bottle is specially designed to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

Dataset-specific Instrument Name	Dionex Ultimate 3000 liquid chromatograph (LC) system
Generic Instrument Name	High-Performance Liquid Chromatograph
Generic Instrument Description	A High-performance liquid chromatograph (HPLC) is a type of liquid chromatography used to separate compounds that are dissolved in solution. HPLC instruments consist of a reservoir of the mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by high pressure pumping of the sample mixture onto a column packed with microspheres coated with the stationary phase. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase.

Dataset-specific Instrument Name	Thermo Scientific iCAP Q ICPMS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset-specific Instrument Name	Bond-Elut ENV solid phase extraction (SPE) columns
Generic Instrument Name	Solid Phase Extraction System
Generic Instrument Description	Solid-phase extraction (SPE) is a solid-liquid extractive technique, by which compounds that are dissolved or suspended in a liquid mixture are separated, isolated or purified, from other compounds in this mixture, according to their physical and chemical properties

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Deployments

NBP2401

Website	https://www.bco-dmo.org/deployment/969543
Platform	RVIB Nathaniel B. Palmer
Report	https://www.bodc.ac.uk/resources/inventories/cruise_inventory/reports/nathanielbpalmer_nbp2401.pdf
Start Date	2023-11-28
End Date	2024-01-28
Description	See more information at: R2R https://www.rvdata.us/search/cruise/NBP2401 BODC https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/18091/ US GEOTRACES https://usgeotraces.ldeo.columbia.edu/content/gp17-ant Description: The U.S. GEOTRACES GP17-ANT expedition departed Punta Arenas, Chile on November 29th, 2023 and arrived in Lyttelton, New Zealand on January 28th, 2024. The cruise took place in the Amundsen Sea aboard the R/V Nathaniel B. Palmer with a team of 35 scientists led by Peter Sedwick (Old Dominion University), Phoebe Lam (University of California, Santa Cruz), and Robert Sherrell (Rutgers University). GP17 was planned as a two-leg expedition, with its first leg (GP17-OCE) as a southward extension of the 2018 GP15 Alaska-Tahiti expedition and this second leg (GP17-ANT) into coastal and shelf waters of Antarctica's Amundsen Sea.

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Project Information

Collaborative Research: US GEOTRACES GP-17-ANT: Molecular speciation of trace element-ligand complexes in the Southern Ocean and Antarctic shelf (GP17-ANT Trace element-ligand complexes)

Coverage: Southern Ocean

NSF Award Abstract:
The supply of iron and other biologically essential trace elements to surface waters is a critical regulator of biological growth in the Southern Ocean. Sea ice volume and the physical dynamics of the Southern Ocean are currently experiencing rapid changes. An understanding of the corresponding changes in metal cycling is needed as these elements are essential for the growth of phytoplankton which plays an important role in modulating atmospheric CO2. One of the major knowledge gaps is understanding how soluble forms of these metals are generated and transported to the surface ocean. Many trace elements are insoluble in seawater and precipitate close to their sources unless they are bound to a dissolved organic molecule, or ligand, that keeps the metal in solution. Little is currently known about what these ligands are, where they come from, or how they affect the reactivity and fate of metals in the Southern Ocean. The study proposed here is designed to identify the organic ligands that bind to metals and determine the ligand sources and reactivity along the Antarctic continental margin.

The proposed project will survey the molecular speciation of six biologically important trace elements (Fe, Cu, Zn. Ni, Co, Mn) along the US GEOTRACES cruise track along the Antarctic shelf in the Amundsen Sea in order to better

understand trace element cycling across the region. The goal of the GEOTRACES expedition is to identify processes and quantify fluxes that control the distributions of trace elements and their isotopes to the Southern Ocean. As part of this effort, the investigators will assess biological ligand production as the ecosystem shifts from low productivity iron-starved conditions in the Antarctic Circumpolar Current to higher productivity along the upwelling continental margin, with a particular focus on assessing production within the Amundsen Sea polynya blooms and sinking organic matter remineralization zones. Second, changes in the accumulation, saturation, and composition of ligands in Circumpolar Deep Water will be measured as the water passes across the Antarctic shelf and receives inputs from sediments and glacial meltwaters. Finally, the role of sea ice on metal-ligand dynamics will be investigated. Metal ligands are a central parameter of numerical ocean models that predict and estimate metal distributions, and results from this project will provide those models with knowledge of the processes that supply ligands and affect ligand concentrations. Two graduate students and undergraduate interns will be supported and trained as part of this project.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Antarctic Sciences (NSF ANT)	ANT-2410011

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